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## Water quality — Determination of selenium —

### Part 2: Method using hydride generation atomic absorption spectrometry (HG-AAS)

*Qualité de l'eau — Dosage du sélénium —*

*Partie 2: Méthode par spectrométrie d'absorption atomique à génération d'hydrures (GH-SAA)*

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## Contents

Page

Foreword .....	v
Introduction.....	vi
1 Scope .....	1
2 Normative references .....	1
3 Principle .....	2
4 Interferences .....	2
5 Reagents and standards.....	3
6 Apparatus and instrumentation .....	5
7 Sampling and sample preparation.....	6
8 Instrumental set up .....	7
9 Procedure .....	7
10 Data analysis and calibration .....	9
11 Expression of results .....	10
12 Test report.....	10
Annex A (informative) Additional information .....	11
Annex B (informative) Schematic flow diagram and signal response .....	12
Annex C (informative) Example of enrichment technique.....	14
Annex D (informative) Precision data .....	16
Bibliography.....	17

## Figures

Figure B.1 — Schematic flow diagram of hydride generation system .....	12
Figure B.2 — Typical signal response from selenium in water sample by atomic absorption spectrometry.....	13

## Tables

Table 1 — Maximum concentration by mass of hydride-forming elements causing no interferences.....	2
Table 2 — Maximum concentration by mass in test solution of interfering heavy metals (valid for flow systems).....	2
Table 3 — Example of standard addition method (volumes adapted for 10 ml volumetric flasks) .....	8
Table D.1 — Precision data .....	16

## Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 17379-2 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

ISO 17379 consists of the following parts, under the general title *Water quality — Determination of selenium*:

- *Part 1: Method using hydride generation atomic fluorescence spectrometry (HG-AFS)*
- *Part 2: Method using hydride generation atomic absorption spectrometry (HG-AAS)*

## Introduction

It is absolutely essential that the tests connected to this part of ISO 17379 are carried out by suitably qualified staff. This method should be used by analysts experienced with the handling of trace elements at very low concentrations.

Inorganic selenium normally occurs in two oxidation states; Se(VI) and Se(IV). It is essential to convert all selenium species to the Se(IV) state prior to generating the hydrides. Selenium(VI) does not form the hydride.

In natural water sources, selenium compounds generally occur in very small quantities, typically less than 1 µg/l. Higher concentrations may be found, for example, in industrial waste water. Selenium occurs naturally in organic and inorganic compounds and may have valency states -2, 0, 4 and 6.

In order to fully decompose all of the selenium compounds, a digestion procedure is necessary. Digestion can only be omitted if it is certain that the selenium in the sample can form a covalent hydride without the necessity of a pre-oxidation step.

The user should be aware that particular problems could require the specification of additional marginal conditions.

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# Water quality — Determination of selenium —

## Part 2:

## Method using hydride generation atomic absorption spectrometry (HG-AAS)

**WARNING** — Persons using this part of ISO 17379 should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

**IMPORTANT** — It is absolutely essential that tests conducted according to this part of ISO 17379 be carried out by suitably trained staff.

### 1 Scope

This part of ISO 17379 specifies a method for the determination of selenium. The method is applicable to drinking water, surface water, ground water and rain water. The application range of this standard is from 0,5 µg/l to 20 µg/l. Samples containing selenium at higher concentrations than the application range can be analysed following appropriate dilution [1]. The method is unlikely to detect organo-selenium compounds.

The sensitivity of this method is dependent on the selected operating conditions.

It is important to use high purity reagents in all cases with minimum levels of selenium. The concentration of the blank solution shall be less than the lower level of interest.

### 2 Normative references

The following reference documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes*

ISO 5667-2, *Water quality — Sampling — Part 2: Guidance on sampling techniques*

ISO 5667-3, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of water samples*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

ISO 8466-2, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 2: Calibration strategy for non-linear second order calibration function*

ISO 15587-1, *Water quality — Digestion for the determination of elements in water — Part 1: Aqua regia digestion*

### 3 Principle

The sample solutions are treated with sodium tetrahydroborate to generate the covalent gaseous hydride ( $\text{SeH}_2$ ). The hydride and excess hydrogen are swept out of the generation vessel into a heated silica glass cell. After atomization the absorbance of selenium is determined at a wavelength of  $\lambda = 196,01 \text{ nm}$ . The procedure is automated by means of an auto sampler and control software.

Other measurement techniques may be applicable providing the performance criteria can be adequately demonstrated by the user laboratory. (See Annex C).

### 4 Interferences

The hydride generation technique is prone to interferences by transition and easily reducible metals. For the majority of natural water samples, this type of interference shall not be significant. The user shall carry out recovery tests on typical waters and also determine the maximum concentrations of potentially interfering elements, using appropriate methods. If such interferences are indicated, the level of interferences shall be assessed by performing spike recoveries.

The reaction conditions in this standard have been chosen to minimise these interferences.

Further information concerning these interferences and the technique are available from the Bibliography.

Elements such as As, Sb, Te, Hg and Sn are also volatilised by this procedure and may cause interferences because of decrease of absorption. These elements will not cause interferences provided the concentrations specified in Table 1 are not exceeded.

**Table 1 — Maximum concentration by mass of hydride-forming elements causing no interferences**

ISO/DIS 17379-2 https://standards.iteh.ai/catalog/standards/sist/8c9ff783-3f79-4b60-bec2-d6008b5fa275/iso-dis-17379-2		Element				
	Unit	As	Sb	Sn	Te	Hg
Concentration by mass of interfering elements in test solution	[mg/l]	1	1	0,1	1	0,1

If these concentrations are exceeded, it may be necessary to use the standard addition method (9.3). Assuming that the selenium content is high enough, an appropriate dilution of the water sample is preferred.

Metals which are readily reduced by sodium tetrahydroborate may also cause interferences. In particular, these include chromium, iron, copper, nickel and lead. If the concentrations of these elements specified in Table 2 are exceeded, a significant decrease of absorption may occur.

**Table 2 — Maximum concentration by mass in test solution of interfering heavy metals (valid for flow systems)**

		Interfering Element				
	Unit	Cr	Fe	Cu	Ni	Pb
Concentration by mass in test solution	[mg/l]	500	500	500	250	100

NOTE If batch systems are used, concentrations which are appreciably lower by mass than those specified in Table 1 and Table 2 may cause interferences.

Since most organic solvents (e.g. alcohols, benzene, ketones) cause severe interferences (signal suppression), they shall be removed by digestion prior to analysis.



## 5 Reagents and standards

### 5.1 General requirements

Reagents may contain selenium as an impurity. All reagents shall have selenium concentrations below that which would result in a selenium blank value for the method being above the lowest level of interest.

Reagents shall be prepared to manufacturer's recommendations using the following series as an example.

**5.2 Water**, complying with grade 1 as specified in ISO 3696 for all sample preparation and dilutions.

**5.3 Hydrochloric acid**,  $\rho(\text{HCl}) = 1,16 \text{ g/ml}$ .

**5.4 Hydrochloric acid**,  $\rho(\text{HCl}) = 1 \text{ mol/l}$ .

**5.5 Sodium tetrahydroborate**,  $\text{NaBH}_4$ .

Available as pellets.

**5.6 Sodium hydroxide**,  $\text{NaOH}$ .

**5.7 Sodium tetrahydroborate solution**,  $\rho(\text{NaBH}_4) = 13 \text{ g/l}$ .

Dissolve  $13,0 \text{ g} \pm 0,1 \text{ g}$  of sodium tetrahydroborate in 500 ml water (5.2) and add  $(4,0 \text{ g} \pm 0,1 \text{ g})$  of sodium hydroxide (5.6). Dilute to 1 000 ml with water (5.2). Filter the solution through a  $0,45 \mu\text{m}$  membrane filter before use.

Prepare on day of use and do not keep in a closed container because of pressure build-up due to hydrogen evolution.

ISO/DIS 17379-2

NOTE 1 Suitably stored sodium tetrahydroborate pellets have a shelf life of 6 months. The concentration of  $\text{NaBH}_4$  will be dependent on the hydride generator manifold and flow-rate conditions. See recommendations of the manufacturer.

NOTE 2 Alternatively smaller volumes can be prepared on a pro rata basis.

**5.8 Nitric acid**,  $\rho(\text{HNO}_3) = 1,40 \text{ g/ml}$ .

NOTE Nitric acid is available both as  $\rho(\text{HNO}_3) = 1,40 \text{ g/ml}$  ( $C(\text{HNO}_3) = 650 \text{ g/kg}$ ) and  $\rho(\text{HNO}_3) = 1,42 \text{ g/ml}$  ( $C(\text{HNO}_3) = 690 \text{ g/kg}$ ).

#### 5.8.1 Nitric acid cleaning mixture

Dilute nitric acid (5.8) with an equal volume of water (5.2) by carefully adding the acid to the water.

### 5.9 Reagent blank

For each 1 000 ml, prepare a solution containing  $400 \text{ ml} \pm 3 \text{ ml}$  of hydrochloric acid (5.3). Dilute to volume with water (5.2).

NOTE On the continuous flow system, the reagent blank solution is run as background. Since the blank solution may contain trace level detectable amounts of selenium it is important that the same reagents are used for sample and standard preparation as well as the preparation of the reagent blank. The analyte signal will be superimposed on the top of this signal once the sample is introduced into the measurement cycle.

### 5.10 Selenium standard solutions

#### 5.10.1 Selenium stock solution A, $\rho(\text{Se}) = 1\,000\text{ mg/l}$ .

Use a quantitative stock solution with an selenium content of  $1\,000\text{ mg/l} \pm 2\text{ mg/l}$ . This solution is considered to be stable for at least one year.

Alternatively, use a stock solution prepared from high purity grade chemicals:

Place 1,094 g of  $\text{Na}_2\text{SeO}_3$  sodium selenite dried for 2 h into a 500 ml in a volumetric flask.

Add 200 ml of water (5.2) and 200 ml of hydrochloric acid (5.4) and dissolve the sodium selenite completely by stirring.

Dilute to 1 l with water (5.2)

#### 5.10.2 Selenium standard solution B, $\rho(\text{Se(IV)}) = 10\text{ mg/l}$ .

Pipette  $1\text{ ml} \pm 0,01\text{ ml}$  of selenium stock solution A (5.10.1) into a 100 ml volumetric flask, add  $40\text{ ml} \pm 0,5\text{ ml}$  of hydrochloric acid (5.3) and fill up to the mark with water (5.2). This solution shall be prepared weekly.

#### 5.10.3 Selenium standard solution C, $\rho(\text{Se(IV)}) = 100\text{ }\mu\text{g/l}$ .

Pipette  $1\text{ ml} \pm 0,01\text{ ml}$  of selenium standard solution B (5.10.2) into a 100 ml volumetric flask, add  $40\text{ ml} \pm 0,5\text{ ml}$  of hydrochloric acid (5.3) and fill up to the mark with water (5.2). This solution shall be prepared weekly.

#### 5.10.4 Selenium standard solution D, $\rho(\text{Se(IV)}) = 10\text{ }\mu\text{g/l}$ .

Pipette  $10\text{ ml} \pm 0,1\text{ ml}$  of selenium standard solution C (5.10.3) into a 100 ml borosilicate volumetric flask. Fill up to the mark with reagent blank solution (5.9). This solution shall be prepared freshly on the day of use.

#### 5.10.5 Selenium standard solution E, $\rho(\text{Se(VI)}) = 1\,000\text{ mg/l}$ .

Dissolve  $2,392\text{ g} \pm 0,002\text{ g}$  of  $\text{Na}_2\text{SeO}_4$  sodium selenite in 500 ml water (5.2) then transfer the solution quantitatively to a 1 000 ml volumetric flask and fill up to the mark with water (5.2).

This standard shall be used to prepare a suitable selenium(VI) standard to check quantitative recovery of selenium(VI). The solution is stable for at least six months.

#### 5.10.6 Selenium calibration solutions

A minimum of five independent calibration solutions shall be used. The calibration is described in ISO 8466-1.

Prepare a minimum of five selenium calibration solutions from the selenium standard solution C (5.11.3) covering the working range of expected selenium concentrations.

For the operating range from  $1\text{ }\mu\text{g/l}$  to  $5\text{ }\mu\text{g/l}$ , for example, proceed e.g. as follows:

Pipette into a series of five 100 ml volumetric flasks  $1\text{ ml} \pm 0,01\text{ ml}$ ,  $2\text{ ml} \pm 0,02\text{ ml}$ ,  $3\text{ ml} \pm 0,03\text{ ml}$ ,  $4\text{ ml} \pm 0,04\text{ ml}$  and  $5\text{ ml} \pm 0,05\text{ ml}$  respectively of selenium standard solution C (5.11.3).

Add 30 ml of hydrochloric acid (5.3).

Dilute to 100 ml with water (5.2) and mix thoroughly.

Allow to stand for at least 2 h before using the solution. This will ensure quantitative reduction of selenium(VI) to selenium(IV).

These calibration solutions contain 1 µg/l, 2 µg/l, 3 µg/l, 4 µg/l and 5 µg/l selenium respectively. They shall be prepared on the day of use.

The use of piston pipettes is permitted and enables the preparation of lower volumes of calibration solutions. The application of dilutors is also allowed.

Once a well established calibration pattern has been established the number of standards used routinely may be reduced. Any such change shall not alter the result obtained from tests or the ranking with other samples.

## 6 Apparatus and instrumentation

The following are set out as guidelines. In general, the manufacturer's instructions shall be followed.

### 6.1 Atomic absorption spectrometer

An atomic absorption spectrometer equipped with a hydride generation system and a heated quartz tube atomizer or a graphite furnace atomizer (preferably equipped with a background correction system) is recommended. Automated flow systems (flow injection analysis (FIA) or continuous flow analysis (CFA)) for hydride generation are suitable and more usual but batch systems are also adequate. The description below follows a continuous flow regime.

#### 6.1.1 Radiation source for the determination of selenium

Use selenium hollow cathode lamps or electrodeless discharge lamps.

### 6.2 Gas supply

Use argon with a grade specified by the manufacturer.

The gas supply shall be with a two stage regulator and the argon supplied at a pressure recommended by the manufacturer.

The use of a gas purifier consisting of activated carbon is recommended.

Nitrogen gas may also be used but will have a reduced sensitivity.

### 6.3 Laboratory ware

#### 6.3.1 General requirements

For the determination of selenium at very low concentrations, contamination and loss are of critical consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment. A clean laboratory work area, designated for trace element sample handling shall be used.

All re-usable laboratory ware in contact with the sample shall be cleaned prior to use.

Laboratory ware shall be soaked in the nitric acid cleaning mixture (5.8.1) for at least 24 h and rinsed five times with water (5.2).

Following this, refill laboratory ware with hydrochloric acid,  $C(\text{HCl}) = 1 \text{ mol/l}$  (5.4) and leave for 24 h.

Disposable (single-use) plastic laboratory ware does not require special cleaning provided that negligible selenium contamination in that material is demonstrated.